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REPORT 7/91

A Preliminary Investigation of the Degradation and Stabilisation
of the Energetic Oxetane Binder PolyNIMMO

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Summary

Information on the structure and functionality of poly(3-nitratomethyl-3-methyloxetane), polyNIMMO, is presented and the properties of binders cured with the isocyanate Desmodur N-100 are considered.

Results from the ageing of crosslinked polyNIMMO are presented and the effects of adding the stabiliser 2-nitrodiphenylamine, (2NDPA), are demonstrated. It is shown that decomposition of the nitrate ester groups of unstabilised polyNIMMO is a major process but the rate of this process is much lower than that observed for nitroglycerin.

Decomposition of the nitrate ester groups in polyNIMMO is accompanied by chain scission of the polyether backbone.

Two effects were observed as a result of adding 1% of 2NDPA, - the rate of nitrate ester breakdown was significantly reduced and the rate of polymer chain scission was greatly retarded. Results indicate that chain scission only becomes significant when the stabiliser has been consumed. Current results show that the stabilised binder still retains its network structure after one year at 60°C.

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1
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CONTENTS

1	Introduction	3
2	Synthesis and Structure	3
3	Binder Cure and properties	4
4	Stability and Stabilisation	5
	4.1 Gas Evolution	5
	4.2 Stabiliser Loss	6
	4.3 Binder Stability	7
5	Conclusions	8
	Figures 1-2	

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1 INTRODUCTION

The solid rocket propellants of the future will be expected to have both high performance and low vulnerability. High performance can currently be achieved by the use of high levels of nitramine. However, traditional nitramine compositions are brittle materials with poor mechanical properties and high vulnerability.

Properties can be improved by employing a polymeric binder such as a polyether, a polyester or hydroxy terminated polybutadiene, but the incorporation of such a binder reduces the energy of the system significantly. To achieve high energy levels without the high solids loading, which increases vulnerability, one approach is to use an energetic binder. A candidate binder which is being evaluated in a number of countries is GAP (glycidyl azide polymer).

Energetic binders based on the polymerisation of nitrated oxetanes is another approach which is being pursued enthusiastically in the UK. The advantage of polyNIMMO is that it will give energetic rubbery binders. The energy comes from the nitrate ester groups and the rubbery properties are due to its aliphatic polyether backbone. In a sense polyNIMMO offers advantages associated with double base and composite propellants. However, it also brings together the different ageing mechanisms associated with these two types of propellant. The breakdown mechanism for double base propellant is degradation of the nitrate ester group. Changes in the polymer network either through crosslinking or scission processes, which can result from oxidation or hydrolysis, are a feature of the chemical breakdown of composite propellant.

The purpose of the work reported here is to identify the processes which determine the long term stability of polyNIMMO binders.

Specific aims are:

- a. to determine the stability of the nitrate ester group in polyNIMMO binders;
- b. to establish the improvements to be gained by adding the stabiliser, 2-NDPA;
- c. to identify the factors which control the long term stability of the polyNIMMO network structure.

2 SYNTHESIS AND STRUCTURE

PolyNIMMO was prepared by the cationic polymerisation of the monomer, 3-nitratomethyl-3-methyloxetane with boron trifluoride etherate/1,4 butanediol as the initiator.

3
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The main features of the polymer structure were established by ^{13}C nuclear magnetic resonance spectroscopy (nmr) and Gel Permeation Chromatography (GPC). The ^{13}C spectra confirmed that the product consisted of a linear polyether produced by the ring opening of the monomer. It also showed that fragments of the 1,4 butanediol co-initiator were incorporated into the polymer, both as chain ends and as in-chain units.

There were three types of polymer end groups. Two types of hydroxyl end group were present, corresponding to terminal 1,4 butanediol units and NIMMO units. Both give rise to primary hydroxyl groups, but whereas the 1,4 butanediol units have reactivities similar to those of the end groups in standard polyethers such as poly(tetramethylene ether glycol), the NIMMO end groups were found to be appreciably less reactive. Since the latter represent well over 50% of the end groups, the polymer hydroxyl end groups are relatively unreactive. The nmr spectra showed that the polymer also contained unreactive ethoxy end groups. In the absence of these groups, the linear prepolymer would have two hydroxyl end groups per chain, and a functionality of two, but the inactive end groups give a functionality of about 1.7 to 1.8. These results are consistent with the cure behaviour described below.

The hydroxyl content was measured from the end group carbons by ^{13}C nmr. The hydroxyl content of a typical batch was about 0.2 mequivs/gm.

GPC indicated that the polymer consisted of a material with a molecular weight of several thousand (nominally $M_w = 7500$), and a polydispersity of about 1.5, together with low molecular weight oligomers. The polymerisation method may be expected to give rise to both linear and cyclic oligomers; results suggest that the oligomer content is less than 5%.

3 BINDER CURE AND PROPERTIES

PolyNIMMO is cured with isocyanates. Theoretically the material is difunctional, but in practice the functionality is less than two. Thus in order to produce a crosslinked binder, it is necessary to introduce components with a functionality greater than two into the cure. This may be done in two ways; either by introducing a polyfunctional hydroxyl components, for example a triol, or by using a polyfunctional isocyanate.

Initially the former approach was used and a series of binders based on polyNIMMO/trimethylol propane (TMP)/MDI was prepared. This produced crosslinked binders, as indicated by physical appearance and sol fraction measurements. As the precise hydroxyl value was unknown, a series of samples with a nominal equivalent ratio of polyNIMMO/TMP/MDI of 1:1:2 was prepared with an assumed value hydroxyl for polyNIMMO ranging from 0.16 to 0.22 mequivs/gm. The samples were cured for 7 days at 60°C, and their sol contents were measured to determine the optimum cure as represented by the minimum sol content. This corresponded to a nominal hydroxyl value of 0.20 mequivs/gm.

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The binders obtained with the polyNIMMO/TMP/MDI were soft and had poor tensile properties.

Binders produced from polyNIMMO and the aliphatic polyisocyanate Desmodur N-100 possessed better rubbery properties and greater mechanical strength.

From dynamic mechanical analysis the T_g of a typical polyNIMMO/Desmodur N-100 binder was found to be -28°C .

The cure of polyNIMMO is slower than that for a conventional polyether. Possible reasons are the lowering of the reactivity of the hydroxyl end groups in the NIMMO end groups due to an electronic influence of the nitrate ester groups and/or to the steric influence of the nitrate and methyl groups on the NIMMO hydroxyl end groups.

Catalysts can be employed to decrease the cure time as required. For example, 0.005% of dibutyl tin dilaurate, added in solvent which is removed under vacuum, gives a complete cure in less than two days at 60°C .

The addition of the nitrate ester stabiliser, 2-nitrodiphenylamine (2-NDPA), at the 1% level did not affect the cure.

4 STABILITY AND STABILISATION

4.1 Gas Evolution

Samples (5g) of polyNIMMO/Desmodur N-100 binder, with and without 1% 2NDPA, were heated for 40 hours at 100°C under vacuum and the quantity of gas evolved was measured using a pressure transducer. The amount of gas produced in this vacuum stability test was 2.09 and 1.11 cc at STP for the unstabilised and stabilised binders respectively.

Thus, even without stabiliser, the gas evolution for polyNIMMO in this test is well below the pass/fail limit of 5 cc at STP. The total amount of gas evolved is about the same as for nitrocellulose, and significantly less than for nitroglycerin, under similar conditions.

To determine the effect of ageing on the vacuum stability of the stabilised polyNIMMO binder, samples were subjected to the vacuum stability test after various periods of storage in air at 60°C . The results in Table 1 show that, over the 9 months of the experiment, the vacuum stability of the binder did not decrease.

TABLE 1 Effect of Time at 60°C on Vacuum Stability Test of Stabilised PolyNIMMO Binder

Time, Months	Vac Stab Test cc at STP
0	1.11
3	0.68
6	0.78
9	0.83

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Results of analysis by GC/MS of the gases evolved at 70 and 100°C on unaged binders are given in Table 2.

TABLE 2 Gases Evolved - PolyNIMMO/Desmodur N-100 Binders, μ l at STP/g/day

Temp °C	Sample	CO ₂	N ₂ O	N ₂	CO	NO	Total
100	Unstabilised	45.1	15.1	132.8	12.6	2.5	208.1
"	Stabilised	13.3	6.7	73.0	2.7	2.6	98.3
70	Unstabilised	0.72	0.13	3.32	0.2	Trace	4.4
"	Stabilised	0.19	0.03	1.74	0.06	Trace	2.0

It is interesting to note that the gas composition at 70°C is similar to that obtained at 100°C.

An Arrhenius plot of log rate against the reciprocal of the absolute temperature for the total gas volumes gave good straight line plots for both the stabilised and unstabilised binders. The activation energy was calculated to be 33 Kcal/mol for both materials.

This activation energy is similar to that found for the decomposition of nitrate esters, and, together with the formation of large amounts of nitrogen, strongly indicates that the gases result from the decomposition of the nitrate ester groups of the polymer.

The fact that the nitrogen content is much greater than the oxides of nitrogen has been found with other nitrate ester systems and is probably due to reaction of the latter with the polymer as they diffuse through the matrix.

4.2 Stabiliser Loss

HPLC analysis of the stabilised binder showed that the 2-NDPA is slowly consumed at 60°C, being first converted to the N-nitroso derivative and then to the dinitro compounds (Tab 3).

From the results of Table 3 it is seen that after 9 months at 60°C the binder has lost less than 20% of its effective stabiliser.

TABLE 3 Effect of Time at 60°C on Stabiliser Content of PolyNIMMO Binder

Time, Months	% 2-NDPA (A)	% N-Nitroso 2-NDPA % (B)	% Effective Stab A + (B x 0.88)
0	0.98	-	0.98
3	0.91	0.10	0.99
6	0.79	0.12	0.90
9	0.69	0.15	0.82

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4.3 Binder Stability

The binder network was characterised by measurement of the sol content of the binder, S; that is the weight fraction of the binder which is removed by extraction with dichloromethane.

Knowing S, the relative crosslink density of the binder can be estimated from the following modified version of the Charlesby-Pinner equation derived in these laboratories.

$$\text{Crosslink density} = \frac{(1-S) [2-(S+\sqrt{S})]}{(S+\sqrt{S})} \quad (1)$$

4.3.1 Unstabilised Binder

Table 4 shows the effect of time and temperature on the sol fraction of a binder. It is seen that the sol content increases with time of heating. That is, the overall degradation process in the polymer network is chain scission. It is also seen that the sol fraction increases more rapidly as the temperature is raised.

TABLE 4 Effect of Time and Temperature on Sol Fraction of PolyNIMMO Binder*

Temperature	Time, Weeks							
°C	0	1	2	8	12	38	52	77
80	0.32	0.45	1.00	-	-	-	-	-
60	0.32	-	-	0.38	1.00	-	-	-
50	0.32	-	-	-	0.40	0.45	0.52	1.00
40	0.32	-	-	-	0.34	0.41	0.42	0.43

*cured with 0.005% tin dibutyl tin dilaurate.

After 2 weeks at 80°C the polymer network is destroyed and the polymer is completely soluble. At 50 and 60°C the same stage is reached after 77 and 12 weeks respectively. From these figures an activations energy for the overall chain scission process of approximately 27 Kcal/mol can be estimated. Using expression (1) to estimate the crosslink density from the measured sol fraction the changes in crosslink density with time for different temperatures can be followed.

Figure 1 shows that the crosslink density decreases with time but the rate, that is the rate of scission, is not constant. Three distinct stages of the degradation process are suggested by Figure 1; an initial scission process, an intermediate period where the rate of scission is low, and the final stage where the rate of scission increases exponentially.

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The results of Table 4 and Figure 1 refer to binder which was unstabilised but contained the cure catalyst dibutyl tin dilaurate. A comparison of the changes in crosslink density of binder with and without catalyst shows that the catalyst marginally accelerates the chain scission process.

4.3.2 Stabilised Binder

The addition of the nitrate ester stabiliser 2-NDPA has a marked effect on the thermal stability of the binder network.

Figure 2 shows the effect of incorporating 1% 2-NDPA on the stability of the binder at 80 and 60°C. The rate of the chain scission process is dramatically reduced by the addition of the 2-NDPA. At 80°C the integrity of the binder network is maintained for 20 weeks. That is a tenfold improvement on the behaviour of the unstabilised binder at the same temperature.

At 60°C the binder with 1% 2-NDPA has shown no change in crosslink density after 55 weeks.

As with the unstabilised binder, Figure 2 suggests that there may be three phases of the scission mechanism with the stabilised material; an initial process followed by a period when the rate of scission is reduced which in turn gives way to rapid breakdown of the network.

The observed shape of the degradation curves can readily be explained in terms of the behaviour expected from materials of this type. Polyethers often contain weak links due to the peroxides formed during preparation and purification steps, which can initiate oxidative chain scission. These could be responsible for the initial reaction phase. The period of reduced chain scission could then be when all these weak links have reacted, and the polymer network is protected by the stabiliser. The final rapid breakdown corresponds to attack on the polymer chain when all the stabiliser has been consumed. It could involve a chain reaction mechanism initiated by breakdown of nitrate ester groups to produce NO_x . If this explanation is correct, then it is clear that the breakdown of the nitrate ester groups, the gas evolution, the loss of stabiliser and the chain scission process are all interrelated. In this context, it is interesting that the stabiliser 2-NDPA has a pronounced inhibiting effect on chain scission, as well as reducing gas evolution. At present, this explanation is speculative, but we are in the process of carrying out further work to check its validity.

5 CONCLUSIONS

This memorandum describes preliminary results on the structure, cure, ageing and stabilisation of the energetic polyoxetane, polyNIMMO. A number of conclusions can be drawn from the work so far.

1 The prepolymer can be cured with the aliphatic polyisocyanate Desmodur N100 to produce binders with good mechanical properties. The optimum cure conditions have been established.

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2 The accelerated ageing shows features of both nitrate ester and polymer network degradation.

3 The rate, the composition of the gas produced, and the activation energy for gas evolution are all typical of nitrates ester decomposition.

4 The rate of gas evolution is not excessive; it is appreciably less than in nitroglycerin.

5 The critical ageing process for binders is chain scission. For unstabilised binders this occurs rapidly at elevated temperatures.

6 The stabiliser 2-NDPA improves the behaviour of the binder considerably. At the 1% level, it has a negligible effect on the cure. It causes a significant decrease in the rate of gas evolution, as is to be expected from a nitrate ester stabiliser. It has an even greater effect on the chain scission process such that the rate of chain scission is very low as long as the 2-NDPA remains.

7 The results suggest that the different ageing mechanisms are interrelated. In particular, the nitrate ester stabiliser 2-NDPA has a larger effect in preventing chain scission than in reducing gas evolution. This may mean that the nitrate ester decomposition is responsible for the chain scission reactions, and the 2-NDPA has a greater effect in preventing the secondary processes responsible for chain scission than in preventing the initial nitrate ester breakdown. It is also possible that the 2-NDPA acts as an antioxidant, thus reducing the contribution of oxidation to chain scission.

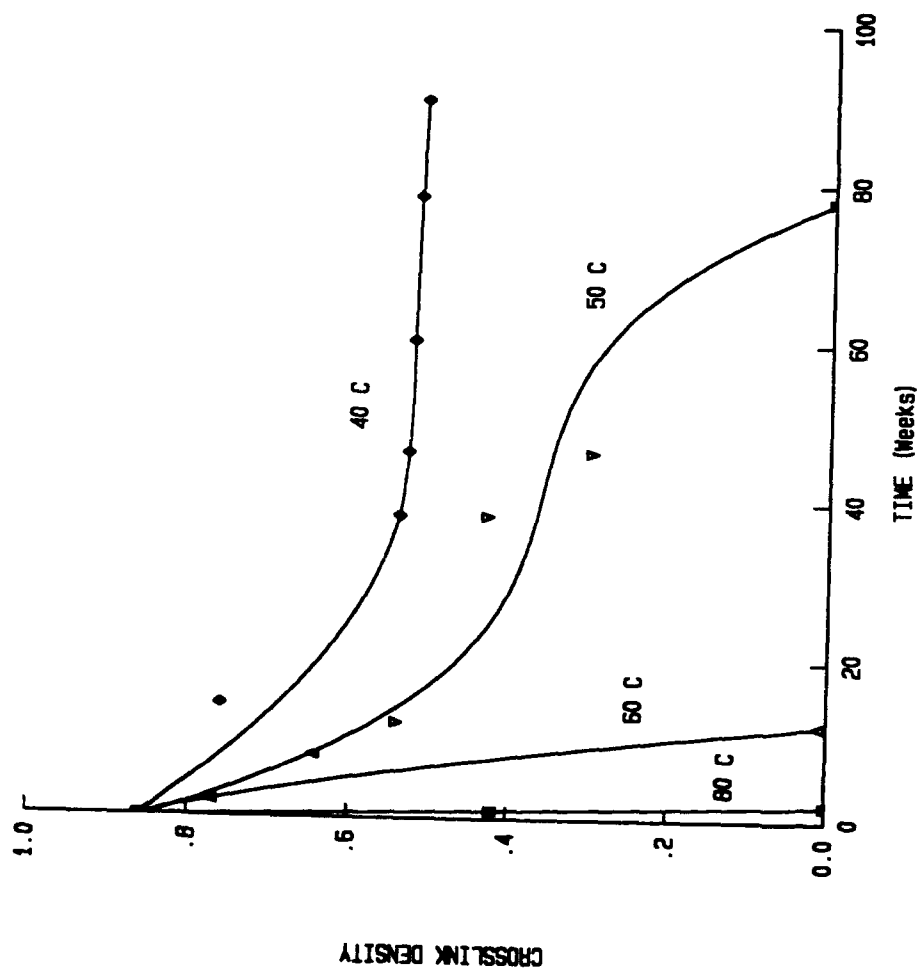


Fig 1 Effect of temperature on crosslink density of poly (NIMMO) binder

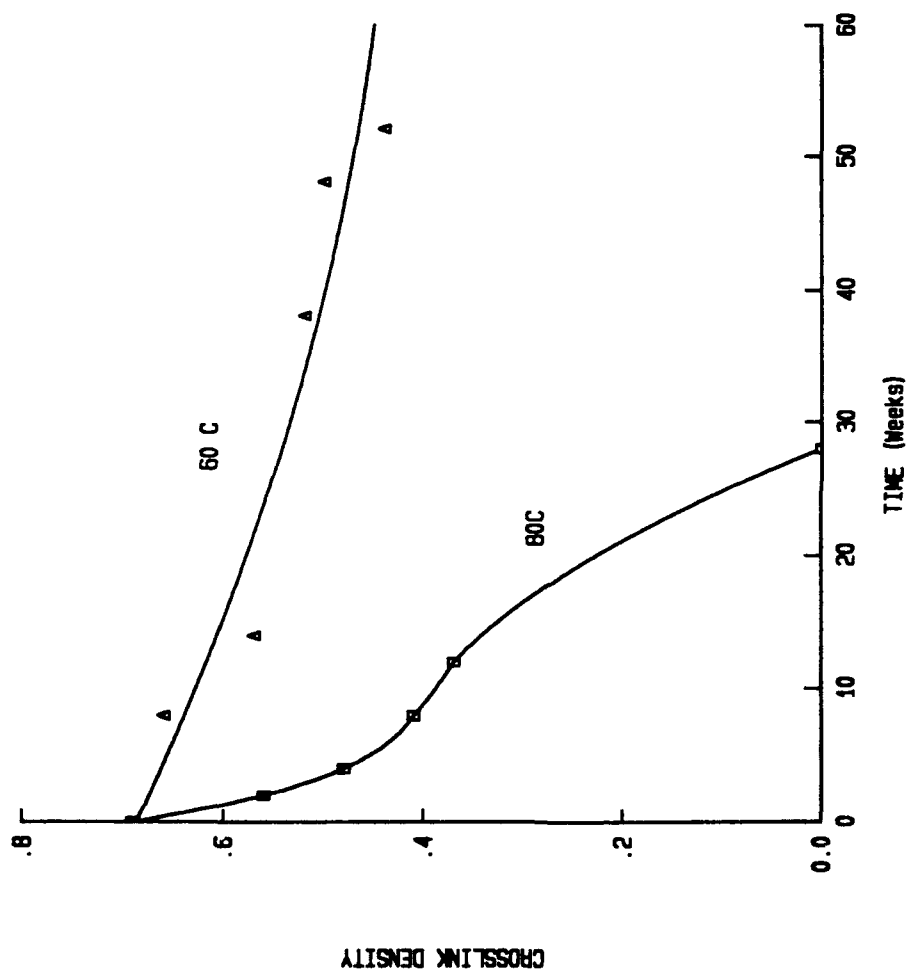


Fig 2 Effect of temperature on poly (NIPMO) binder with 1% 2-NDA

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